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Structural and optical properties of ZnS nanostructured films synthesized *via* RF-magnetron sputtering technique

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Abstract : Nanostructured ZnS thin films have been synthesized by radio frequency magnetron sputtering technique X-ray diffraction and selected area electron diffraction studies confirmed the formation of nanocrystalline cubic phase of ZnS in the films The particle size calculated from the XRD patterns of the thin films was found in the range 2 06–4 86 nm TEM micrographs of the thin films revealed the manifestation of ZnS nanoparticles with sizes lying in the range 3 00–5 83 nm UV-Vis-NIR spectrophotometric measurements showed that the films are highly transparent (~90 %) in the wavelength range 500–2600 nm The absorption edge showed a blue shift The direct allowed bandgaps was found in the range 3 89–4 44 eV The room temperature photoluminescence spectra of the films showed two peaks centered around 315 nm and 450 nm We assigned the first peak due to bandgap transitions while the latter due to sulfur vacancy in the films The composition analysis by energy dispersive X-rays also supported the existence of sulfur deficiency in the films The thicknesses of the films were in the range 260–350 nm depending on the deposition time.

Keywords : Nanostructured films, RF-sputtering, TEM, photoluminescence

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1. Introduction

In recent years nanostructured materials have gained special interest due to their novel properties and possibilities of many applications. Previously, one-dimensional ZnS nanostructures have been reported, including ZnS nanowires by liquid crystal template, micelle template, thermal evaporation using Au catalyst *etc.* Recently, ZnS nanobelts synthesis by chemical bath deposition (CBD) within the self-organized pores of polyvinyl alcohol (PVA) was reported by us [1]. ZnS nanoparticles have also been reported [2] *via* chemical routes without capping agent, using thioglycerol as capping agent [3] and using sodium dioctyl sulfosuccinate as a surfactant [4]. But to our knowledge there is no report on the synthesis of ZnS nanoparticles in thin film form *via* radio frequency magnetron sputtering without using any matrix and its detail studies of optical properties. In this paper we report the size dependent optical properties of ZnS nanoparticles synthesized *via* RF-magnetron sputtering without using any capping agents or matrix.

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2. Experimental

Zinc sulfide (ZnS) target was fabricated by taking a suitable aluminium holder (5 cm dia.) and compacting the ZnS polycrystalline powder (99.99%, Aldrich) by applying suitable hydrostatic pressure (~100 kg/cm^2). Detail of experimental procedure can be found elsewhere [5]. The films were synthesized at room temperature (298 K) on glass and Si substrates for 10–30 min. The sputtering parameters for deposition of thin films were : effective RF-power : 170 Watt, electrode distance : 3 cm, sputtering gas : Ar, gas pressure : 0.1 mbar.

3. Results and discussion

3.1. Nanostructural studies :

The nanostructures of the films were studied at room temperature by a using a transmission electron microscope (TEM, Hitachi-H600). The micrographs of ZnS nanoparticles have been shown in Figure 1(a) and (b). Presence of ZnS nanoparticles is clearly visible in TEM bright field images and corresponding diffraction patterns of the film consists of several concentric rings. From the diameter of the rings, we calculated the inter-planer spacing (d_{hkl}) values, which correspond to reflection from (111), (200), (220) and (311) planes of cubic ZnS with a_0 = 5.406 Å. The average particles sizes obtained from TEM micrograph were in the range of 3.0–5.83 nm.

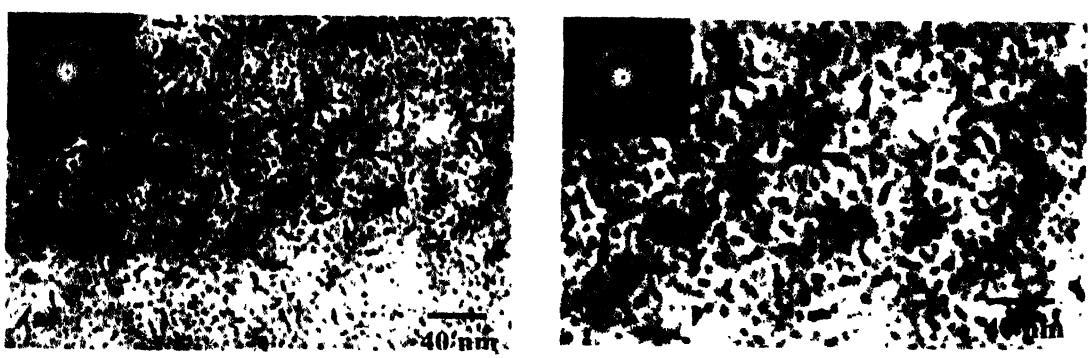

Figure 1. TEM micrographs of ZnS for different deposition time (a) 10 min, (b) 20 min and Inset: corresponding SAED patterns.

Figure 2 shows the X-ray diffraction (XRD) patterns of ZnS thin films. One peak of ZnS has been obtained due to diffraction form (111) plane of cubic ZnS. The particle size (L) of the deposited films have been obtained from standared Scherrer relations. The interplanner spacing (d_{hkl}) corresponding to XRD peaks, TEM measurement and joint committee for powder diffraction studies (JCPDS) card [6] matched well.

The composition of the films was determined by energy dispersive X-ray analysis (EDX, JEOL JSM 6300 Oxford-7582)). The Zn : S in the target material was ~1 : 1. The final sulfur concentration in the films decreases with the increase in deposition

time. The final composition inside the film for different deposition time is as shown in Table 1.

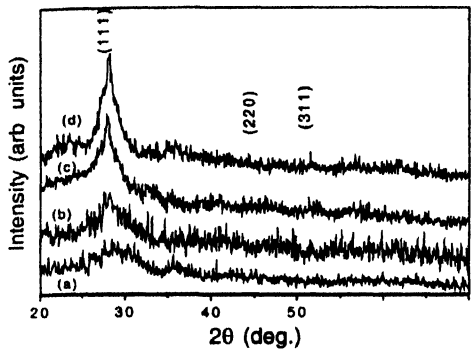

Figure 2. XRD patterns of thin ZnS films deposited on glass substrate for different deposition time (a) 10 min, (b) 15 min, (c) 20 min and (d) 25 min.

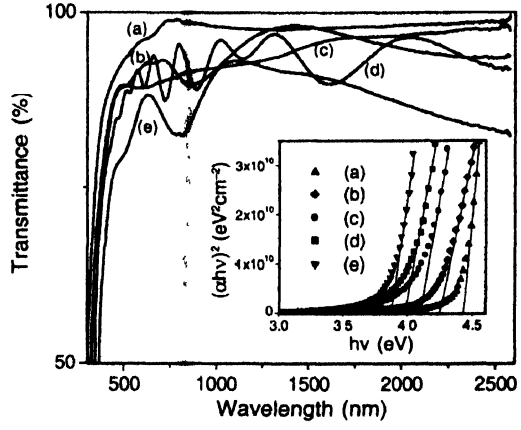

Figure 3. Transmittance spectra for different deposition time and inset: corresponding $(\alpha h\nu)^2$ *vs.* $h\nu$ plots.

Table 1. The direct bandgap (E_g), particle size (L) from shift of E_g and Zn/S ratios obtained from EDX for different deposition time (d_t):

Sample name	d_t (min)	E_g (eV)	L (nm)	Zn/S
(a)	10	4.44	3.23	1.09
(b)	15	4.26	3.72	1.12
(c)	20	4.09	4.36	1.15
(d)	25	3.98	4.92	1.19
(e)	30	3.89	5.6	1.26

3.2. Optical studies :

The transmission *vs.* wavelength traces for different ZnS thin films have been recorded as shown in Figure 3. The direct bandgap values lie in the range 3.89 eV to 4.44 eV calculated from $(\alpha h\nu)^2$ *vs.* $h\nu$ plots as shown in inset of Figure 3. The direct bandgap values of the films are higher than that of bulk value of ZnS (3.6 eV) because of quantum confinement of carriers in ZnS nanocrystals.

The shift of band gap might also be utilized in determining the crystal radius (r) using reported standard relation [7]. The values of direct bandgap, and particle size from shift of direct bandgap for different deposition time are shown in Table 2. It is clear from the table that the direct bandgap decreases with the increase of deposition time and the particle size increases with the increase of deposition time. It can also be noticed that that there is some mismatch of particle size determined from XRD, TEM and optical method. Particle size determined from XRD is always found to be smaller than that measured by TEM or optical method because from XRD we get length of coherence in the grains which do not include grain boundaries.

Table 2. The comparison of particle size obtained from TEM (L_{TEM}), XRD (L_{XRD}) and shift of direct optical bandgap ($L_{Optical}$) and corresponding film thickness (F_t) for different deposition time (d_t)

Sample name	d_t (min)	F_t (nm)	L_{TEM} (nm)	L_{XRD} (nm)	$L_{Optical}$ (nm)
(a)	10	260	3 00	2 06	3 23
(b)	15	330	3 52	2 65	3 72
(c)	20	410	4 60	3 26	4 36
(d)	25	490	5 31	4 07	4 92
(e)	30	530	5 83	4 86	5 6

3 3 Photoluminescence studies

Photoluminescence (PL) spectra, measured at room temperature (300 K) of the nanocrystalline ZnS thin films deposited on glass substrates are shown in Figure 4. All the plots contain two peaks centered at 315 nm and at 450 nm The excitation wavelength was 200 nm (xenon lamp, 100 W) It is evident from Figure 4 that the position of 2nd peak is not shifted with the variation of particle sizes Hence, the photoluminescence in this region is due to the presence of sulfur vacancies in the lattice, which is also previously reported by Sooklal *et al* [8] The sulfur deficiency in the synthesized nanocrystalline ZnS films was also confirmed from EDX measurements of the samples. Also it was observed that with the increase of deposition time, the intensity of the PL peak increased

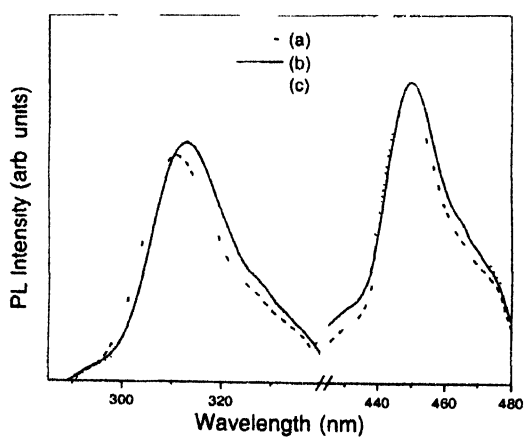

Figure 4. PL-spectra of nano-ZnS thin films for different deposition time (a) 10 min, (b) 20 min and (c) 30 min

This is due to the fact that with the increase of deposition time sulfur deficiency increases which is supported by the EDX results. The other PL peak appeared at ~315 nm and from Figure 4 it is clear that the position of this peaks changes with the deposition time which indicate the peak position depends on the particle size. This peak is assigned due to the band-to-band transition of nanocrystalline ZnS. As the bandgap energy depends on the particle size, the position of the peak changes accordingly. In the present study trap related emission was not observed, most

probably this emission is obstructed by the grain boundaries owing to compactness of nanograins.

4. Conclusion

Nanoparticles of ZnS have been successfully synthesized by *rf*-magnetron sputtering technique. TEM micrographs of the films revealed the manifestation of ZnS nanoparticles with sizes lying in the range 3.0–5.83 nm. From the transmittance and reflectance spectra of the films the direct bandgap values have been calculated and they lie in the range 3.89–4.44 eV. The room temperature photoluminescence spectra of the films showed two peaks centered around 315 nm and 450 nm. EDX measurements confirmed the sulfur vacancy in the films.

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